

Air corona removal of phenols

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Exposure to the neutral activated species of an a.c. point-to-plane type corona discharge in air of aqueous alkaline solutions of phenol and substituted phenols (pentachlorophenol, triiodo 2,4,6 phenol and picric acid) leads to the oxidative destruction of the solutes up to the CO₂ state in the case of phenol. The influence of the discharge parameters, such as the current intensity, is considered. The destruction of phenates follows overall pseudo first-order kinetics, and the kinetic constants are linearly dependent on the current. A scheme for the degradation kinetics is proposed involving a multistep mechanism, and the occurrence of dihydroxybenzenes as reaction intermediates is suggested. Applications of corona treatment to waste waters may be considered as a versatile method for the elimination of toxic chemicals and the purification of industrial waters.

1. Introduction

International and national regulations are becoming increasingly severe concerning the quality of the environment and the amount of pollutants discharged in industrial effluents. Thus it becomes necessary from both the legal and ecological points of view to control carefully industrial wastes and to develop new techniques to treat the pollutants.

Phenols occupy a prominent place among the pollutants of ground waters. Each pollutant toxicity varies according to the number and the nature of the substituents on the parent molecule. For instance, phenol does not exhibit high toxicity against *Esch. Coli* [1] and is known to be easily biodegradable. Its occurrence in water gives an unpleasant taste even at low concentrations (i.e., 0.1 to 0.2 mg dm⁻³). However, nitrophenols are not bio-degradable, and in particular trinitrophenol is quite stable, except when used as an explosive. Trichloro-2,4,5 phenol is involved as a precursor in the formation of dioxin which was responsible for the Seveso disaster. These three particular examples show that phenols, which are able to form chloroderivatives, belong to a family of chemicals with large ranges of toxicities involved in numerous industrial processes in various fields.

Various methods have been proposed to eliminate phenols from waste waters. These may be conventionally classified according to three methods: physical, chemical and biochemical treatments. The physical treatments include adsorption of phenols on activated carbon chromatography and solvent extraction. The chemical treatments are based on oxidation reactions with strong oxidizers, such as chlorine and its derivatives (i.e., chlorine dioxide or hypochlorite), ozone and hydrogen peroxide. Some of these are expensive (e.g., ClO₂, O₃ or H₂O₂); others involve chlorine either as a byproduct or as

the starting material. Biological treatments involve the formation and development, in the aerated phenol solution, of numerous bacteria (belonging mainly to the pseudomonas family) in addition to algae and other microorganisms. The efficiency of this low-cost treatment is close to 95%, which makes it industrially attractive. However, the biochemical treatments fail to destroy some phenol derivatives such as nitrophenols which remain in muds and city effluents.

We report here on a new method to remove phenol and substituted phenols from aqueous solutions which can be easily adapted to the treatment of waste waters. This method is based on the oxidizing properties of an electric discharge burning in humid air.

2. Experimental details

The device involved a Pyrex glass reactor which allowed discharges under controlled conditions, such as the nature of the plasma gas, the gas flow and the electrode gap. The stainless steel electrodes (i.e., a point and a ring) were connected to the H.V. and to earth respectively. The electric power was supplied by a 15 kHz a.c. generator providing a stabilized current. The tested solutions were placed in a 20 ml beaker under the ring.

The solutions were prepared from commercially available analytical grade chemicals (Aldrich), except for the potassium picrate which was prepared at the laboratory.

The concentrations of the solutes were determined immediately after the treatment; and for most of the cases direct spectrophotometric measurements were preferred. However, the concentration of phenol was measured after reaction of phenol with amino-4 pyridine in the presence of ferricyanide according to standard procedures.

3. Corona discharge

3.1. General features

When two conductors of different shapes (such as plane and point electrodes) are disposed in a convenient gaseous atmosphere and raised to a convenient voltage difference a corona discharge takes place between them. The point electrode is raised to the H.V. and the plane electrode is earthed. This discharge is characterized by a particular set of self-sustained electric conditions, provided the voltage difference is greater than the discharge threshold and less than the breakdown potential. This potential difference usually ranges between 3 and 10 kV depending on the electrode gap.

Lack of symmetry between the electrodes leads to several important consequences. The so-called active electrode, characterized by a smaller head radius, corresponds to the higher electric field density. The interactions between the gaseous matter and the electric field are maximum in the surroundings of this electrode. They induce electric and optical phenomena such as excitation, ionization of the gaseous species and light emission by radiative deexcitation. Hence, at the head of the active electrode, we find the ionization volume where electrons and both ionized species and neutral species (i.e., atoms, radicals and molecules) are present. The neutral species are gathered in the drift volume lying between the electrodes. They are not affected by the electrostatic field and also the charged species with the same polarity as that of the active electrode. In an a.c. discharge, we can consider that only the neutral species are present in the drift zone between the electrodes. The corona discharge is then characterized by a mass transfer flow called the electric wind which is directed from the ionization volume around the active electrode towards the low density electric field electrode. The transferred matter is either in the fundamental state or in some electronically/vibrationally excited state which makes the particles highly reactive. A general scheme of the process is given in Fig. 1.

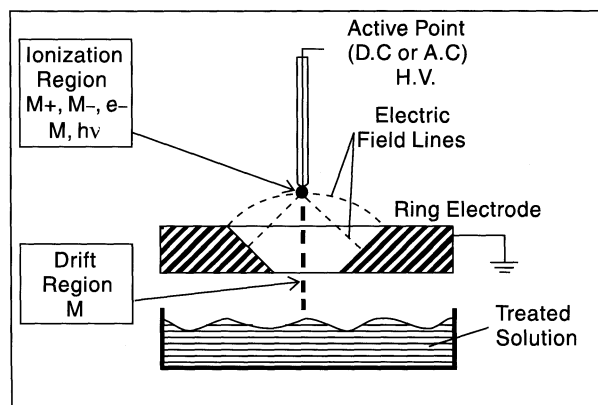


Fig. 1. Sketch of the device and distribution of the main species in an a.c. corona discharge.

Since we are interested [2,3] in the chemical properties of the neutral species, it is of fundamental importance to filter the charged species, both the electrons and the ions. This may be done in the case of a d. c. discharge by means of grid acting as an ion trap and transparent to the neutral species. We used an improved device involving an earthed ring electrode, the inner diameter of the ring being large enough to avoid diffraction of the neutral species. For an a.c. discharge, the occurrence of charged species in the electrode gap may be reasonably ignored. The device used in this study possesses the advantages of both systems.

Information on the general uses of coronas are given in [4–8].

3.2. Nature of the species present in a discharge in humid air

Peyrous [9,10] investigated ozone production by means of corona discharges of both polarities in air or oxygen and demonstrated the occurrence of nitrogen oxides with ozone; he later confirmed [10] Eliasson's results [11] by numerical simulation and considered the occurrence of OH° and HO_2° radicals among others.

The a.c. corona treatment performed in our laboratory according to standard conditions of aqueous solutions of particular solutes (i.e., 4-dimethylnitrosoaniline, aminonaphtylhydrazide or safranin T), which are well known as OH° selective reagents, yielded positive results and confirmed the occurrence of the relevant species. For a negative corona operated at atmospheric pressure, Schramm et al. [12] performed mass spectrometry experiments and found that CO_3^- , O_3^- and to a lesser extent NO_3^- were present at the anode, with the relevant water clusters. In a positive corona, Skalny [13] found that NO^+ and O_2^+ are prominent with the corresponding water clusters. In addition, O_2^+ clusters react with water to yield solvated protons and OH° radicals.

The authors then concentrated on the influence of water on the species formed. Peyrous [14] focused on low pressure positive coronas and confirmed the formation of H_3O^+ and N_2H^+ in addition to NO^+ and O_2^+ . He pointed out that N_2^+ or H_2O^+ may then react with water to yield OH° . A simulation [15] was developed and confirmed that O_3 , H_2O_2 , HNO_2 , NO_2 , NO_x , HNO_3 , NO^- are the main species in humid air. The radicals H° , OH° , HO_2° reach their maximum concentration progressively faster with the increase in humidity.

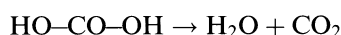
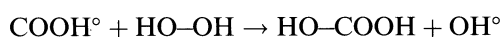
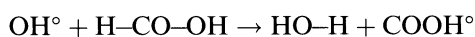
3.3. Chemical properties of the neutral species

The neutral species generated in a corona discharge (i.e., atoms, radicals and molecules) are in their fundamental state or raised to an electronically/vibrationally excited state. The relevant new state of the electrons on the HOMO orbitals assigns to these species new properties and possible new reaction

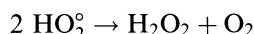
pathways. For example, molecular oxygen has the structure of a diradical in the fundamental state, since two odd electrons (of parallel spins) are in the two π^* orbitals. When raised to the $1\Delta_g$ excited state, one of the π^* orbitals is filled with an electron pair and the other is empty, which assigns to dioxygen the properties of a Lewis acid, as illustrated by the Diels–Adler reaction with conjugated dienes. In the triplet excited state, each π^* orbital is filled with one odd electron, and the relevant spins are opposed, which gives again to the excited molecule the properties of a diradical.

A large number of the neutral species generated in a discharge are radicals. We have focused on their chemical properties since we consider these species to be responsible for the main effects observed in most of the surface treatments of materials resulting from their exposure to electric discharge. For example, the treatment of polymer materials by oxygenated plasmas (air or pure oxygen) often leads to the breaking of the C–C bonds and the formation of terminal –COOH carboxylic acid groups, and this is related to the oxidation of the carbon chain.

Particular attention must be devoted to the OH° and O_2H° radicals because they are generated by a discharge in water saturated air and, second, because they are able to react with water and solutes as they are present in the plasma phase. Exposure of water to radiations yields solvated electrons, solvated protons, OH° , H° and hydrogen peroxide by a series of physical, physicochemical and chemical processes. The hydroperoxide radical O_2H° results from the reaction of H° with O_2 . A particular feature is the strong oxidizing properties of OH° and O_2H° . The normal potential E° of the $\text{OH}^\circ/\text{OH}^-$ system is 2.02 V vs NHE in the gas phase and 2.85 V vs NHE in aqueous solution. Both values are greater than the potential of water ($\text{O}_2/\text{H}_2\text{O}$) and most organic systems. The reactivity of these species has been known for a long time [16], since the oxidation of formic acid occurs through a chain mechanism involving the formation of intermediate radicals which are able to react with hydrogen peroxide and yield an unstable peroxyacid which decomposes yielding carbon dioxide:



HO_2° is also a strong oxidizer since the value of the normal potential of the system HO_2° , $\text{H}^+/\text{H}_2\text{O}_2$ is 1.5 V vs NHE. However, it is considered to be unreactive with organics, and this is attributed to the reaction:



Hence, we cannot consider HO_2° as the major reactive species involved in the oxidation of inorganic or organic solutes.

4. Results and discussion

4.1. Treatment of phenol

Acid and basic solutions of phenol were exposed to the discharge, and in both cases the concentration of the solute decreased with exposure time, for a fixed current and ultimately yielded carbon dioxide.

4.1.1. Treatment in basic media. In basic media (i.e., in 0.01 M NaOH solution) the hydroxy ions concentration does not change significantly despite the acid effect of the plasma treatment: the pH remains greater than 10, and phenol in the phenate form. The u.v.–visible absorption spectra of the treated solutions were recorded (Fig. 2). Their change with the treatment time suggests a complicated mechanism, since a series of absorption bands increases then decreases, as illustrated by the bands centred at 318 nm and 263 nm. The intensity of some bands remains fairly constant for more than half an hour (e.g., the 287 nm band); that of other bands decreases and especially the phenate band at 235 nm [17,18]. This suggests

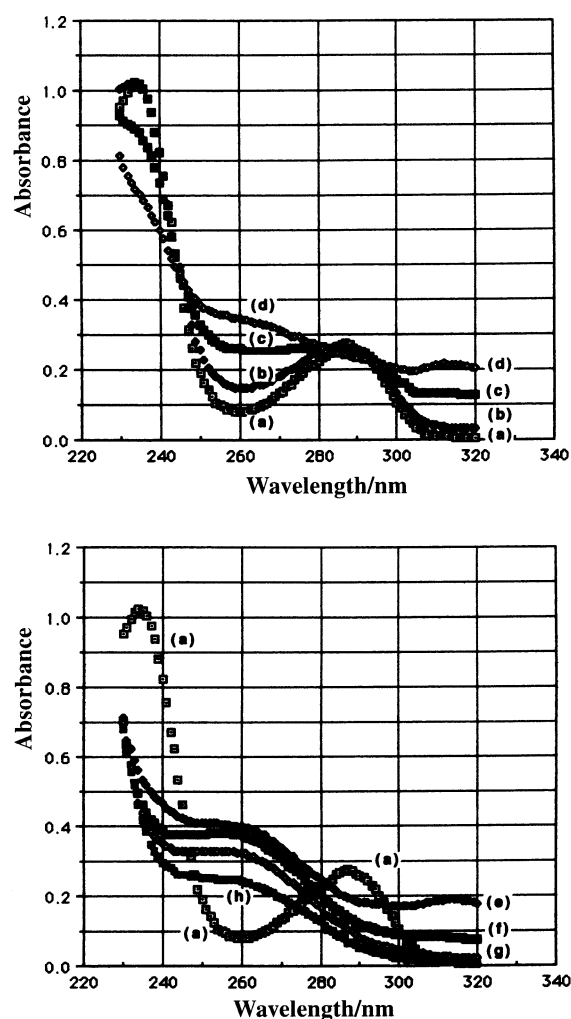
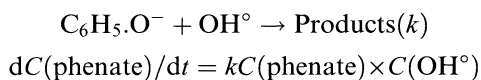


Fig. 2. Absorption spectra of a (10^{-4} M) phenate solution exposed to the neutral species of an a.c. discharge in humid air (current: 44 μA) at times, t : (a) 0, (b) 5, (c) 16, (d) 30, (e) 45, (f) 60, (g) 80 and (h) 130 min.

multistep kinetics. However, the phenate concentration decreases exponentially with treatment time t , and the plot of $\ln |A_\infty - A|$ against t , where A refers to the absorbance of the solution at 235 nm, is linear for more than 120 minutes. Thus, the overall degradation of phenate obeys pseudo first-order kinetics, and the kinetic constant, k , is given by the slope of the relevant straight line.

Experiments with different currents led to similar observations and conclusions. The kinetic constant, k , is a linearly increasing function of the current (Fig. 3) with a slope of $0.52 \times 10^{-3} \text{ min}^{-1} \mu\text{A}^{-1}$. This result is in agreement with the basic assumption involving a radical R° (i.e., HO_2° , or more likely OH°) as the main oxidizing agent generated by the discharge and responsible for the degradation of phenol. The rate determining steps are related to the disappearance of phenate:

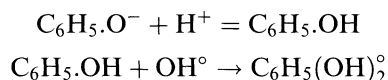


and the relevant kinetics are pseudo first-order provided $C(\text{OH}^\circ)$ is directly dependent on the current, that is, on the electron flux: $C(\text{OH}^\circ) = KI$ which is a reasonable assumption since we know that the excited species are generated by the discharge.

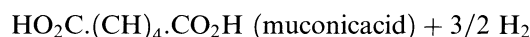
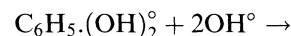
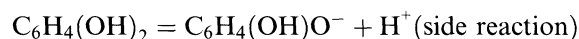
The mechanism may be partly inferred from examination of the absorbance spectra during treatment (Fig. 2(a) and (b)). For the first half-hour an absorption peak appears close to 260 nm with an intense band at 210 nm. The latter band may be related to phenol (211 nm and 275 nm, according to [17,18]) and with the formation of nitrite/nitrate (absorption peaks at 210 nm and 202 nm, respectively [17]): this suggests that a rapid equilibrium between phenate and phenol takes place in the primary steps. The band at 260 nm increases then decreases: this may be attributed to the formation, followed by the destruction, of dihydroxy-1,4 benzene or, more likely,

to that of the relevant monoanion (absorption bands at 264, 312 and 325 nm [19]). Thus the evolution of the absorption spectra with time suggests the occurrence of diphenols as intermediates, since the addition of OH° to a benzene ring has been known for a long time from radiolysis studies and since OH° also induces the oxidation of hydroquinone. Besides, the high alkalinity of the reactive medium induces an equilibrium between the molecular and the anionic forms.

The reaction mechanism may be proposed as follows:



yielding mainly the (1,4) and (1,2) derivatives. The formation of the dihydroxycyclohexadienyl radical is followed by water elimination to yield the phenoxy radical $\text{C}_6\text{H}_5\text{O}^\circ$ (absorption peak at 290 nm [20]) according to a mechanism already discussed [20].



$\text{C}_6\text{H}_5(\text{OH})$ is also oxidized in a series of monoacids: the concentrations of hexanoic, iso valeric, *i*- and *n*- butyric acids give a maximum for treatments shorter than half an hour as shown by ion chromatography, while that of lighter acids (e.g., acetic and propionic acids) give a maximum after 1.5 h treatment. Specific tests for CO_2 were found positive.

4.1.2. Treatment in acid media. In an acid medium, the modification of the absorption spectra of the phenol solutions is less complicated, and the relevant intermediates can be identified on the basis of the preceding discussion. The reaction scheme remains valid, except that the conjugated bases for the dihydroxybenzenes need not to be considered.

4.2. Treatment of substituted phenols

The general character of the plasma treatment is demonstrated on a series of substituted phenols, and we selected halogenated phenols as examples of major pollutants and the trinitro-2,4,6 phenol as a non biodegradable chemical.

Alkaline solutions of triiodo 2,4,6 phenol were treated by the neutral species of an a.c. corona discharge under the same conditions as the phenate solutions. The absorbance at 319 nm decreases as the exposure time increases, so that the removal of phenol can be considered as a pseudo first order reaction. The kinetic constants were again found to be dependent on the current (Tables 1 and 2; Fig. 3).

Similar conclusions arise from treatments of the various phenates examined. The absorption peaks at 320 nm and 365 nm were selected to follow the decrease in the pentachlorophenate and picrate concentrations, respectively.

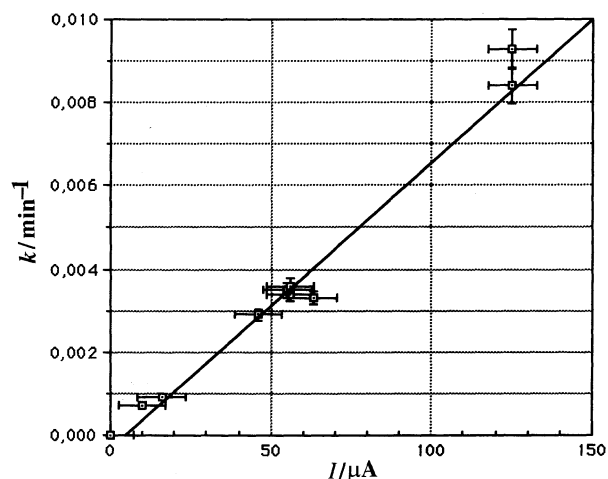


Fig. 3. Variations of the pseudo first-order constant $k(\text{min}^{-1})$ with the current intensity $I(\mu\text{A})$ of the discharge for the a.c. corona treatment of 10^{-4} M picrate solutions.

Table 1. Pseudo first-order kinetic constants k (min^{-1}) for various substituted phenols

$I/\mu\text{A}$	$k(a)$	$k(b)$	$k(c)$	$k(d)$	$k(e)$
0.0	0.0000	0.0000	0.0000	0.0000	0.0000
10.0				0.0007	
16.0				0.0009	
20.0	0.0104	0.0035			
20.1			0.0050		0.0060
25.0					0.0073
30.0	0.0162				0.0086
31.0					0.0082
40.0	0.0208	0.0071			0.0120
46.0				0.0029	0.0157
50.0		0.0094	0.0128		0.0160
55.0				0.0035	
56.0				0.0034	
56.0				0.0036	
63.0				0.0033	
125.0				0.0084	
125.0				0.0093	

(a) unsubstituted; (b) 2, 4, 6-triiodo; (c) 2, 4, 6-trimethyl; (d) 2, 4, 6-trinitro; (e) pentachloro, as a function of the current $I(\mu\text{A})$ of the discharge.

In addition, the sonochemical degradation of pentachlorophenolate in carbon dioxide has been recently examined [21]. The authors demonstrated that the active species responsible for the reaction were the same as in a corona discharge, that is, the OH° radicals, which are also generated in the ultrasonic treatment of an aqueous solution.

On the basis of the slopes of the relevant k against I plots which are gathered in Table 2, it is possible to compare the various phenols examined. The parent molecule (or rather the parent ion) is destroyed the most rapidly, followed by the pentachloro phenate, the triiodo 2,4,6 phenate and the picrate and this order of reactivity may be related to the steric hindrance of the substituent groups determined on the basis of the covalent radii for H, Cl, I and NO_2 . In addition, test spots showed cleavage of the carbon-halogen bondings, so that halogenides X^- are present in the solution, which is consequent with the bonding energies C-X (339 kJ for chlorine; 218 kJ for iodine),

Table 2. Dependence of the kinetic constant k (min^{-1}) on the current intensity $I(\mu\text{A})$ for the examined phenates: $k = a + bI$

Substituent	$10^4 a$	$10^4 b$	r^2
(1) phenol	0.34286	5.2514	0.999
(2) 2, 4, 6-triiodo	-1.0847	1.8576	0.998
(4) 2, 4, 6-trinitro	-3.1375	0.70937	0.981
(5) pentachloro	-7.0911	3.2826	0.977

C – H (435 kJ) and C – C (518 kJ bonding energy in benzene).

5. Conclusions

This work demonstrates that the complete degradation of phenol and substituted phenols in aqueous solutions can be achieved by means of exposure to the flux of the activated neutral species generated in an a.c. corona discharge burning in air. Phenols are oxidized up to CO_2 ; they are destroyed according to pseudo first order kinetics; the relevant constants are linear functions of the current involved in the a.c. discharge and depend on the steric hindrance of the substituent group. It is shown that the electric discharge technique provides a new alternative technique, competing with other methods, for the treatment of toxic wastes.

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